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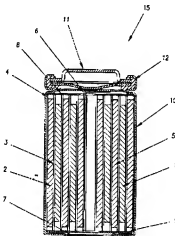
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(54) **METHODE DE REDUCTION DE LA SURFACE EFFECTIVE DE
POUDRES CARBONEES**

(54) **METHOD FOR REDUCING THE SURFACE AREA OF
CARBONACEOUS POWDERS**



(57) La surface de poudres charbonneuses peut être réduite par le mélange d'une petite quantité de pétrole ou de goudron avec la poudre charbonneuse et le mélange est ensuite soumis à la pyrolyse. La poudre charbonneuse est enduite de produits de la décomposition du goudron et le revêtement peut avoir une surface sensiblement inférieure à celle de la poudre charbonneuse initiale. De petites quantités de goudron pyrolysé sont en présence et les principales propriétés de la poudre charbonneuse sont pratiquement inchangées. La méthode convient particulièrement à la réduction de la surface des poudres d'anode charbonneuses destinées à être utilisées dans les batteries au lithium rechargeables à électrolyte non aqueux, ce qui accroît le degré de sécurité de ces batteries.

(57) The surface area of carbonaceous powders can be reduced by mixing a small amount of petroleum or coal tar pitch with the carbonaceous powder and pyrolyzing the mixture. The carbonaceous powder becomes coated with decomposition products of the pitch and the coating can have substantially lower surface area than the original carbonaceous powder. Small amounts of pyrolyzed pitch are involved and the bulk properties of the carbonaceous powder remain virtually unaffected. The method is particularly suitable for reducing the surface area of carbonaceous anode powders for use in non-aqueous rechargeable lithium ion batteries and thereby improves the safety of the batteries.

ABSTRACT

The surface area of carbonaceous powders can be reduced by mixing a small amount of petroleum or coal tar pitch with the carbonaceous powder and pyrolyzing the mixture. The carbonaceous powder becomes coated with decomposition products of the pitch and the coating can have substantially lower surface area than the original carbonaceous powder. Small amounts of pyrolyzed pitch are involved and the bulk properties of the carbonaceous powder remain virtually unaffected. The method is particularly suitable for reducing the surface area of carbonaceous anode powders for use in non-aqueous rechargeable lithium ion batteries and thereby improves the safety of the batteries.

METHOD FOR REDUCING THE SURFACE AREA
OF CARBONACEOUS POWDERS

FIELD OF THE INVENTION

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This invention pertains to methods for reducing the surface area of carbonaceous powders. Specifically, it pertains to methods for reducing the surface area of carbonaceous anode powders for use in non-aqueous rechargeable lithium ion batteries and thereby improving the safety of the batteries.

BACKGROUND OF THE INVENTION

15 Carbonaceous powders exist in many different forms, including amorphous carbons (eg. soot), cokes, graphites, and speciality carbons. These powders are used widely throughout many varied industries. In many applications, high surface area carbonaceous powders are desired to provide a maximum reactive surface (eg. activated char-
20 coals). Alternatively, it can be desirable to employ powders with minimal surface area. Since smaller particles present larger surfaces per unit volume or mass, the use of the largest particles possible is generally preferred in minimizing surface area. Use of powder with a uniform
25 particle size (diameter) can be most preferred. Spherically shaped particles theoretically can provide the lowest possible surface area for a given particle size if the particle surface is smooth. Spherically shaped carbonaceous powders that are relatively smooth are commercially
30 available as speciality products (eg. mesocarbon microbeads, hereinafter referred to as MCMB). However, in practice, it can be difficult to achieve surface area values close to the theoretical. There is usually some
35 significant surface roughness on the particles and often there can be significant variation amongst different production batches.

Lithium ion rechargeable batteries have been available commercially since about 1991 and represent a preferred

rechargeable power source for many consumer electronics applications. These batteries are characterized by a large energy density (Wh/L) and high operating voltage (typically above 3½ volts). Such batteries use two different insertion compounds with ample capacity for reversible lithium insertion but with differing lithium insertion potential for the active cathode and anode materials. At this time, a lithium transition metal oxide (eg. LiCoO_2 , LiNiO_2 , LiMn_2O_4) is usually employed as the cathode material and a carbonaceous compound (eg. coke, graphite, hard disordered carbon) is usually used as the anode material.

The relatively low ionic conductivity of the typical non-aqueous electrolytes employed in lithium ion batteries makes it necessary to use thin electrodes (of order of 100 micrometer thick) in order to allow battery operation at reasonable rates. Additionally, the diffusion coefficients for lithium in the typical electrode material is not so great. As a consequence, electrodes of the active insertion compounds are typically made of small particles (eg. 20 micrometers in size).

The use of small particles not only desirably increases the battery rate capability but also unfortunately increases the amount of and/or rate of certain undesirable chemical reactions that occur on the particle surfaces. For instance, an irreversible loss of lithium occurs on the carbonaceous anode surface in order to form a protective passivation film against further decomposition. Thus, the more surface, the more the irreversible loss of lithium capacity. Additionally, the safety level of lithium ion batteries can be higher when low surface area electrode materials are used. For instance, U.S. patent number 5,246,201 discloses the effect of the surface area of a LiNiO_2 electrode on battery behaviour during thermal abuse.

The spherically shaped mesocarbon microbeads carbonaceous powder, known as MCMB (a product of Osaka Gas), has been advantageously employed by many in the art as the

active anode material in lithium ion batteries (see, for example, European patent application number EP 474,183). As a result of its uniform size and low surface area for a given particle size, such MCMB powder can allow high electrode packing densities and good battery rate capability while still presenting a minimal surface area for undesirable chemical reactions.

Generally, it is known in the art that pyrolyzing organic precursors, such as benzene, in the presence of carbonaceous compounds can modify the surface conditions of the carbonaceous compound, including the surface area thereof. However, it is not possible to predict whether such pyrolysis will result in a high surface area or 'fluffy' deposit or, alternatively, result in a smooth low surface area deposit.

In published Japanese patent application number JP05-307959, Mitsubishi discloses the use of a substantial amount of pyrolyzed pitch (preferably 30 to 40% of the total weight) to agglomerate and coat the particles of a core material (an active carbonaceous anode powder), thereby producing a coated agglomerate anode powder with certain advantageous properties. The coated agglomerates are substantially larger in size than the original core particles and have, as expected, a smaller surface area. In an example therein, core particles that were 6 micrometers in diameter were treated in this manner and were then ground up into agglomerates that were about 20 micrometers in diameter. A reduction in geometric surface area is thus inherently expected.

SUMMARY OF THE INVENTION

A method has been discovered for reducing the surface area of carbonaceous powders in general and specifically for reducing the surface area of electrode materials used in rechargeable lithium batteries. The method involves pyrolyzing an amount of petroleum or coal tar pitch in the

vicinity of the carbonaceous powder. The carbonaceous powder becomes coated with decomposition products of the pitch and the coating can have substantially lower surface area than the original carbonaceous powder.

- 5 Specifically, an amount of petroleum or coal tar pitch is mixed with the carbonaceous powder. The mixture is then pyrolyzed in an inert atmosphere at a temperature above the decomposition temperature of the pitch. Some mild agglomeration may occur as a result of the pyrolysis.
- 10 Consequently, any agglomerates are broken up such that the particle size distribution of the coated carbonaceous powder is essentially unchanged by the pyrolysis or the coating.

- The method can be successfully used on carbonaceous
- 15 powders such as spherical graphite, flaky graphite, or hard disordered carbon. The average particle size of the carbonaceous powders can be in a range from about 20 to 75 micrometers and the surface area of the carbonaceous powders before pyrolysis can typically be in a range from
- 20 about 1 to 210 m²/g. The method of the invention can reduce the surface area substantially such that the surface area of the coated carbonaceous powder after pyrolysis may be in a range from about 0.3 to 12 m²/g.

- The amount of pitch employed can range from about 7
- 25 to 33% wt. of the weight of the carbonaceous powder. Depending on the pyrolysis yield, the pitch decomposition product coating can then be in a weight range from about 2 to 9% wt. of the weight of the carbonaceous powder. Since these relatively small amounts can result in a substantial
- 30 surface area reduction, the bulk properties of the coated carbonaceous powder remain largely unaffected by the coating.

- The pyrolysis can be performed at a temperature from about 1000 to 2650°C, and for times of about 30 minutes.
- 35 Ramping rates of about 10°C per minute can also be employed.

It can be particularly advantageous to apply the method of the invention in the construction of certain batteries. For instance, as mentioned above, the spherical carbonaceous powder MCMB is commonly employed as the active
5 anode material in lithium ion batteries. A particular particle size of MCMB may be selected for purposes of obtaining high electrode packing densities and good battery rate capability. However, the surface area of commercial MCMB is generally somewhat higher than that expected for
10 smooth spherical particles of similar size. Additionally, the MCMB surface area may occasionally be substantially higher than that expected for equivalent smooth particles. (The reason for this is unknown, but it may relate to scaleup and/or control difficulties during manufacture of
15 the MCMB.) Thus, there is generally some theoretical possibility for the reduction of the surface area of the MCMB and, often, there is substantial possibility for such reduction.

20 We have discovered that by using the method of the invention, the surface area of such anode powders can indeed be reduced thereby still providing the desired advantages for that particular particle size selection of powder while simultaneously minimizing any disadvantages
25 arising from chemical reactions at the powder surface.

The battery can therefore be a non-aqueous rechargeable lithium ion battery and can have a carbonaceous powder electrode comprising spherical graphite. A preferred average particle size for such battery electrode
30 powders is about 20 micrometers and the surface area of such powders before pyrolysis treatment can be about $2 \text{ m}^2/\text{g}$.

The use of a minimal amount of pitch may be desirable in such applications in order to obtain a substantial surface area reduction without significantly altering the
35 bulk properties of the anode powder. Thus, the amount of pitch can be about 7% wt. of the weight of the carbonaceous powder. Depending on the pyrolysis yield, the pitch

decomposition product coating can then be from about 2 to 4% wt. of the weight of the carbonaceous powder. Such pyrolysis treatment can reduce the surface area such that the coated carbonaceous powder after pyrolysis is less than
5 about 0.5 m²/g.

BRIEF DESCRIPTION OF THE DRAWINGS

In drawings which illustrate specific embodiments of
10 the invention, but which should not be construed as restricting the spirit or scope of the invention in any way:

Figure 1 depicts a cross-sectional view of a conventional cylindrical spiral-wound lithium ion battery.
15

Figures 2a and b show the temperature versus time data during hot box testing of the batteries having different anode surface area in the Battery Examples.
20

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS OF THE INVENTION

We have discovered that the surface area of carbonaceous powders can be reduced by pyrolyzing an amount of petroleum or coal tar pitch in the vicinity of the carbonaceous powder such that the powder becomes coated with decomposition products of the pitch. Volatile components of the pitch apparently deposit on the powder and fill
25 'cracks' or other surface irregularities during the pyrolysis such that the final decomposed pitch components unexpectedly form a smooth, thin coating on the powder. This coating can have a substantially lower surface area than the original carbonaceous powder.

35 Generally, according to the invention, a carbonaceous powder is first identified as having a surface area that is significantly higher than that desired for a particular

application. Additionally, of course, the surface area must also be significantly higher than the theoretical lower limit for the particle shape and size distribution for that powder. The method then comprises mixing/dispersing a suitable amount of petroleum or coal tar pitch with the carbonaceous powder and pyrolyzing the mixture. The preferred amount of pitch is selected on the basis of overall results from a few non-inventive empirical trials.

- The pyrolysis is performed in an inert atmosphere at a temperature above the decomposition temperature of the pitch. Petroleum and coal tar pitch contain mainly high molecular weight aromatic compounds which do not vaporize below about 200°C (for example, see 'Carbon and Graphite Handbook', edited by C.L. Mandell, published by John Wiley and Sons, 1968). Typical pyrolysis temperatures are substantially higher, about 900°C and even up to about 3000°C. However, the structure of the bulk carbonaceous powder itself can be significantly affected by treatment temperatures as high as the latter 3000°C. Thus, unless it is desirable to additionally anneal or graphitize the carbonaceous powder as well as reduce its surface area, a pyrolysis temperature close to the former 900°C is generally employed. A typical suitable pyrolysis time is about 30 minutes and a typical suitable temperature ramping rate, which can be achieved using common furnaces, is about 10 °C per minute.

- Following the pyrolysis, some mild agglomeration may be encouraged. The extent of any agglomeration will depend in part on the amount of pitch employed. Any such agglomerates are easily broken up by a mild grinding operation such that the original particle size distribution of the carbonaceous powder is essentially maintained.

- The method can be successfully used on a variety of carbonaceous powders including spherical graphite (eg. MCMB), flaky graphite, and hard disordered carbon. The average particle size of such powders can be in a range from about 20 to 75 micrometers with surface areas that are

typically in a range from about 1 to 210 m²/g. For use in the method, preferred amounts of pitch can be from about 7 to 33% of the weight of the carbonaceous powder with a resulting pyrolyzed coating weight from about 2 to 9% of the weight of the powder, depending on the yield. Reductions in surface area below 12 m²/g and down to 0.3 m²/g can be expected to be achieved.

In battery applications, a similar method is employed in the preparation of carbonaceous powders for use as an electrode material. A preferred application is in the manufacture of commercial lithium ion batteries. These batteries come in a variety of sizes and formats, including coin cell and prismatic constructions. Figure 1 shows a typical construction of a conventional cylindrical spiral-wound battery lithium ion battery. Therein, a jelly roll 4 is created by spirally winding a cathode foil 1, an anode foil 2, and two microporous polyolefin sheets 3 that act as separators.

Cathode foils for the jelly-roll are prepared by applying a mixture of a suitable powdered cathode material, such as LiCoO₂, a binder, and a conductive dilutant onto a thin aluminum foil. Typically, the application method first involves dissolving the binder in a suitable liquid carrier. Then, a slurry is prepared using this solution plus the other powdered solid components. The slurry is then coated uniformly onto the substrate foil. Afterwards, the carrier solvent is evaporated away. Generally, both sides of the aluminum foil substrate are coated in this manner and subsequently the cathode foil is calendered.

Anode foils are prepared in a like manner except that a reduced surface area powdered carbonaceous insertion compound prepared by the method of the invention (typically about 20 micron size) is used instead of the cathode material and thin copper foil is usually used instead of aluminum. Anode foils are often slightly wider than the cathode foils in order to ensure that anode foil is always opposite cathode foil.

The jelly roll 4 is inserted into a conventional battery can 10. A header 11 and gasket 12 are used to seal the battery 15. The header may include safety devices if desired (eg. overpressure vent, positive temperature coefficient device, and/or a pressure activated electrical disconnect device). The external surface of the header 11 is used as the positive terminal, while the external surface of the can 10 serves as the negative terminal.

Appropriate cathode tab 6 and anode tab 7 connections are made to connect the internal electrodes to the external terminals. Appropriate insulating pieces 8 and 9 may be inserted to prevent the possibility of internal shorting. Prior to crimping the header 11 to the can 10 in order to seal the battery, a suitable non-aqueous electrolyte 5 is added to fill the porous spaces in the jelly roll 4. Suitable electrolytes include those having such lithium salts as LiPF_6 or LiBF_4 dissolved in mixtures of linear and/or cyclic carbonate solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) solvents.

The header 11 is then crimped to the can 10. Lastly, an electrical conditioning step involving at least a single charging of the battery is usually performed next as part of the assembly process.

As mentioned earlier, the spherical carbonaceous powder MCMB is commonly employed as the active anode material in lithium ion batteries. MCMB with a nominally uniform particle size is often chosen for purposes of obtaining high anode packing densities and good battery rate capability. Also, the lowest surface area possible for the anode material is desirable, since it can provide the greatest level of safety in certain circumstances. For instance, during high temperature abusive conditions, the non-aqueous electrolyte in these batteries can react exothermically with the lithium in the anode at a reaction rate determined in part by the anode surface area. The threshold value at which a thermal runaway occurs can be

significantly raised with a reduction in the reactive surface area of the anode.

However, the surface area of commercial MCMB is generally, and not unexpectedly, somewhat higher than the theoretical value for any given nominal particle size. Also, we have found that the surface area of an occasional batch of commercial MCMB may be substantially higher than usual for reasons unknown. Consequently, the method of the invention can be useful in reducing, to some extent, the surface area of an MCMB batch generally and can be particularly useful in 'correcting' the surface area of any such occasional high surface area batch.

MCMB having an average particle size of about 20 micrometers may be desirable for lithium ion battery anode applications. The surface area of such powder can typically be about 2 m²/g. The use of a minimal amount of pitch while still obtaining a substantial surface area reduction is generally desirable. Thus, the amount of pitch can be about 7% of the weight of the carbonaceous powder which can result in a decomposition product coating from about 2 to 4% of the weight of the powder, depending on pyrolysis yield. Such pyrolysis treatment can reduce the surface area markedly to less than about 0.5 m²/g, without significantly affecting the particle size distribution of the powder.

The following Examples are provided to illustrate certain aspects of the invention but should not be construed as limiting in any way.

30 Inventive Examples

We have been successful in reducing the surface areas of several carbonaceous powders using the method of the invention as summarized below in Table 1. The powders used were: MCMB (a product of Osaka Gas), a flaky graphite denoted KS75TM (a product of Lonza), a flaky graphite denoted SFG75TM (a product of Lonza), and a hard disordered

carbon prepared by pyrolyzing Plenco 11760™ resin (a product of Plastics Engineering Co.) at 800°C in argon. An amount of either petroleum pitch or coal tar pitch (indicated as a % by weight of the powder) was added to the
5 powder and mixed therewith. The mixture was then pyrolyzed at a temperature and for a time as indicated.

In order to determine the amount of decomposition product remaining on each powder after pyrolysis, samples of pure petroleum and coal tar pitch were pyrolyzed under
10 similar conditions in a thermal gravimetric analyzer. The yield in each case after pyrolysis was about 28% and 50% by weight respectively. A similar yield for each pitch type is expected in these inventive examples.

Samples 1 to 5 agglomerated slightly and the agglomerates were broken up in the following manner. First, the
15 pyrolyzed product was passed through a mesh screen (140 size mesh for samples 1 to 3, and 80 size mesh for samples 4 and 5). Greater than 80% by weight went through easily on this initial screening. The remainder was lightly
20 ground using a manual mortar and pestle. The lightly ground agglomerates then went through a second screening using the same mesh. Greater than 95% of the pyrolyzed product in total passed through the screen. The screened powder was then used to determine the characteristics in
25 Table 1.

Sample 6 agglomerated somewhat more than the other samples. Significantly more grinding was performed using a manual mortar and pestle until >95% by weight went
30 through a 140 size mesh screen. The significant grinding of sample 6 was evidently excessive for purposes of breaking up agglomerates only, based on the increase in the average particle size after treatment.

Surface areas were determined by BET, a standard
35 nitrogen adsorption technique, using a commercial analytical machine made by Quantachrome. Before measuring, all

samples were outgassed by preheating at 150°C under pure nitrogen for 30 minutes.

Particle size distributions were determined via laser diffraction methods using a commercial analytical machine made by Horiba. In Table 1, only the average particle size of each sample is reported for comparison. In samples 1 to 5, there was no substantial change in particle size distribution as evidenced by little change in the average particle size. In sample 6, the powder after treatment and excessive grinding actually showed a marked reduction in average particle size. Nonetheless, data for this sample has been included since it still shows a marked reduction in surface area as well.

In all instances, the surface area was reduced by a factor of over 2 without a significant increase in average particle size. The surface area of the spherically shaped MCMC was reduced a factor of over 4 in sample 1. Sample 6 showed an order of magnitude reduction in surface area.

Table 1. Surface area and average particle size data for Inventive samples before and after pyrolysis treatment.

Sample No.	Powder Type	Pitch Type	% Pitch added by weight	Temp. (°C)	Time (hours)	Surface area before treatment (m ² /g)	Average particle size before treatment (μm)	Surface area after treatment (m ² /g)	Average particle size after treatment (μm)
1	MCMB	Coal tar	7	2650	6	1.55	23.0	0.34	26.3
2	MCMB	Petroleum	7	2650	6	1.97	22.8	0.49	25.3
3	MCMB (annealed @2650°C)	Coal tar	7	1000	0.5	1.51	22.6	0.41	24.9
4	KS75	Petroleum	15.5	1050	2	7.5	26.8	1.6	31.3
5	SPG75	Petroleum	15.5	1050	2	3.5	35.7	1.1	37.8
6	Pyrolyzed Phenolic resin	Petroleum	33	1000	2	208	73.4	11.4	42.4

Comparative Example

A sample of MCMB similar to samples 1 and 2 above
5 (Table 1) was obtained and was determined to have a BET
surface area before pyrolysis treatment of $1.1 \text{ m}^2/\text{g}$. Then,
7% by weight of table sugar was mixed with this sample and
the mixture was pyrolyzed at 1000°C for 0.5 hours. As in
the Inventive Examples above, slight agglomeration of the
10 powder occurred. The agglomerates were broken up in the
same manner as samples 1 to 3. The surface area after
pyrolysis treatment was found to be $20.2 \text{ m}^2/\text{g}$, that is,
substantially higher than that of the starting powder.

This example demonstrates that not every pyrolyzed
15 organic precursor suitably reduces the surface area of
certain carbonaceous powders, particularly that of MCMB, a
powder having a relatively low surface area to begin with.

Battery Examples

20 18650 size cylindrical batteries (18 mm diameter, 650
mm height) were fabricated as described in the preceding
and shown generally in Figure 1. Cathodes comprised a
mixture of LiCoO_2 powder, graphite conductive dilutant, and
25 polyvinylidene fluoride (PVDF) binder that was uniformly
coated on both sides of a thin aluminum foil. Anodes were
made using either Inventive Sample No. 1 after treatment
or, for comparison, Sample No. 3 before treatment (ie. a
material similar to Inventive Sample No. 1 but without a
30 pyrolyzed pitch coating). The active anode material was
mixed with Super S (trademark of Ensagri) carbon black and
PVDF binder and uniformly coated on thin copper foil to
prepare an anode. Celgard® 2400 microporous polypropylene
film was used for the separators 3. The electrolyte 5 used
35 was a solution of 1M LiPF_6 salt dissolved in a solvent
mixture of ethylene carbonate (EC), ethyl methyl carbonate
(EMC), and diethyl carbonate (DEC) in a volume ratio of

30/50/20 respectively. All batteries were made in the same manner except that some anodes were pitch treated according to the method of the invention and thus had lower surface area.

- 5 After assembly, the batteries were electrically conditioned (ie. a controlled charging) and cycled once under similar conditions. Both types of battery showed similar capacities and rate capabilities.

- 10 A representative fully charged battery made with each anode was then subjected to a thermal abuse test. Batteries were placed in a convection oven set at 150°C and the battery skin temperature versus time was monitored. Figures 2a and b show the temperature versus time data for the Comparative battery (made with Sample No. 3 before treatment, namely an untreated higher surface area MCMB) and the Inventive battery (made with Sample No. 1 after treatment, namely a pitch treated lower surface area MCMB) respectively. As can be seen in Figure 2a, the Comparative battery skin temperature continues to climb above the 150°C set point of the oven as a result of exothermic reactions taking place in the battery. Thermal runaway occurs just before 0.7 hours into the test whereupon the battery vents violently with flame. The temperature is seen to spike upwards and then falls as the battery cools after burning.
- 25 In comparison, the Inventive Battery as seen in Figure 2b, shows much less heating from internal exothermic reactions and does not undergo thermal runaway. (The drop in the temperature plot at about 1.2 hours is due to the opening of the pressure relief vent of the battery.)

- 30 This comparative example demonstrates the safety advantage associated with use of lower surface area anode material.

- As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the invention is to be construed
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in accordance with the substance defined by the following
claims.

WHAT IS CLAIMED IS:

1. A method for reducing the surface area of a carbonaceous powder comprising:
 - 5 mixing an amount of petroleum or coal tar pitch with the carbonaceous powder to produce a mixture; and
 - pyrolyzing the mixture in an inert atmosphere at a temperature above the decomposition temperature of the pitch thereby coating the carbonaceous powder with carbonaceous decomposition products of the pitch; the particle
 - 10 size distribution of the coated carbonaceous powder being essentially unchanged by the coating.
2. A method as claimed in claim 1 including breaking up
- 15 agglomerates which may form as a result of the pyrolysis.
3. A method as claimed in claim 1 wherein the carbonaceous powder is selected from the group consisting of spherical graphite, flaky graphite, and hard disordered
- 20 carbon.
4. A method as claimed in claim 1 wherein the amount of pitch is from about 7 to 33% weight of the weight of the carbonaceous powder.
- 25 5. A method as claimed in claim 1 wherein the pyrolyzing is performed at a temperature from about 1000 to 2650°C.
6. A method as claimed in claim 1 wherein the pyrolyzing
- 30 is performed for about 30 minutes.
7. A method as claimed in claim 1 wherein the mixture after the pyrolyzing is cooled at a rate of about 10°C per minute.

8. A method as claimed in claim 1 wherein the carbonaceous decomposition product coating is from about 2 to 9% weight of the weight of the carbonaceous powder.
- 5 9. A method as claimed in claim 1 wherein the average particle size is in a range from about 20 to 75 micrometers.
- 10 10. A method as claimed in claim 1 wherein the surface area of the carbonaceous powder before pyrolysis is in a range from about 1 to 210 m²/g.
11. A method as claimed in claim 9 wherein the surface area of the coated carbonaceous powder after pyrolysis is
- 15 in a range from about 0.3 to 12 m²/g.
12. A method of making a battery having an electrode of a carbonaceous powder wherein the preparation of the electrode comprises:
- 20 mixing an amount of petroleum or coal tar pitch with the carbonaceous powder; and
- pyrolyzing the mixture in an inert atmosphere at a temperature above the decomposition temperature of the pitch thereby coating the carbonaceous powder with carbonaceous decomposition products of the pitch; the particle
- 25 size distribution of the coated carbonaceous electrode powder being essentially unchanged by the coating, whereby the surface area of the coated carbonaceous electrode powder is reduced by the coating.
- 30 13. A method as claimed in claim 12 including breaking up agglomerates which may form as a result of the pyrolysis.
14. A method of making a battery as claimed in claim 12
- 35 wherein the battery is a non-aqueous rechargeable lithium ion battery.

15. A method as claimed in claim 14 wherein the carbonaceous powder is spherical graphite.
16. A method as claimed in claim 14 wherein the amount of
5 pitch is about 7% weight of the weight of the carbonaceous powder.
17. A method as claimed in claim 14 wherein the carbonaceous decomposition product coating is from about 2 to 4%
10 weight of the weight of the carbonaceous powder.
18. A method as claimed in claim 14 wherein the average particle size is about 20 micrometers.
- 15 19. A method as claimed in claim 14 wherein the surface area of the carbonaceous powder before pyrolysis is about 2 m²/g.
- 20 20. A method as claimed in claim 14 wherein the surface area of the coated carbonaceous powder after pyrolysis is less than about 0.5 m²/g.
21. A method for reducing the surface area of a carbonaceous powder comprising:
25 pyrolyzing a mixture of petroleum or coal tar pitch with carbonaceous powder in an inert atmosphere at a temperature above the decomposition temperature of the pitch thereby coating the carbonaceous powder with carbonaceous decomposition products of the pitch; the particle
30 size distribution of the coated carbonaceous powder being essentially unchanged by the coating.
22. A method of making an electrode of a carbonaceous powder suitable for use in a battery comprising:
35 pyrolyzing a mixture of petroleum or coal tar pitch and carbonaceous powder in an inert atmosphere at a temperature above the decomposition temperature of the pitch

thereby coating the carbonaceous powder with carbonaceous decomposition products of the pitch; the particle size distribution of the coated carbonaceous powder being essentially unchanged by the coating.

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23. A carbonaceous powder with reduced surface area comprising a pyrolyzed mixture of petroleum or coal tar pitch and the carbonaceous powder; said mixture having been pyrolyzed in an inert atmosphere at a temperature above the decomposition temperature of the pitch whereby the carbonaceous powder is coated with carbonaceous decomposition products of the pitch; the surface area of the coated carbonaceous powder being reduced by the coating and the particle size distribution of the coated carbonaceous powder being essentially unchanged by the coating.

24. A rechargeable lithium battery comprising:
- (a) a battery casing;
 - (b) an anode constructed from a carbonaceous powder prepared by pyrolyzing a mixture of petroleum or coal tar pitch and carbonaceous powder in an inert atmosphere at a temperature above the decomposition temperature of the pitch thereby coating the carbonaceous powder with carbonaceous decomposition products of the pitch; the surface area of the coated carbonaceous powder being reduced by the coating and the particle size distribution of the coated carbonaceous powder being essentially unchanged by the coating;
 - (c) a cathode; and
 - (d) an electrolyte which permits lithium atoms to be reciprocally exchanged between the anode and the cathode.

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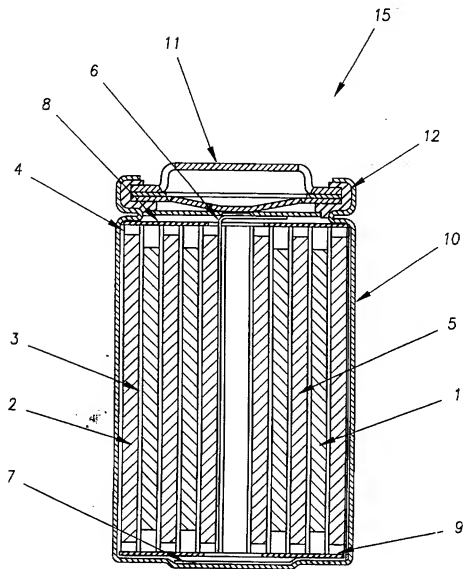


FIGURE 1

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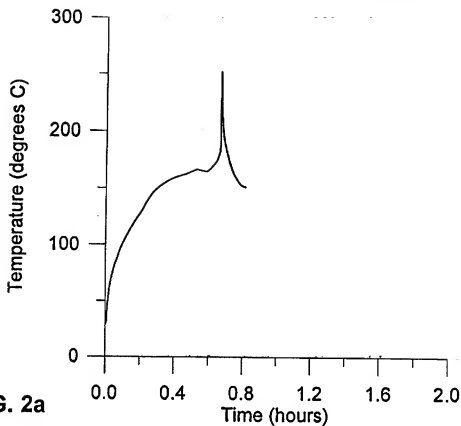


FIG. 2a

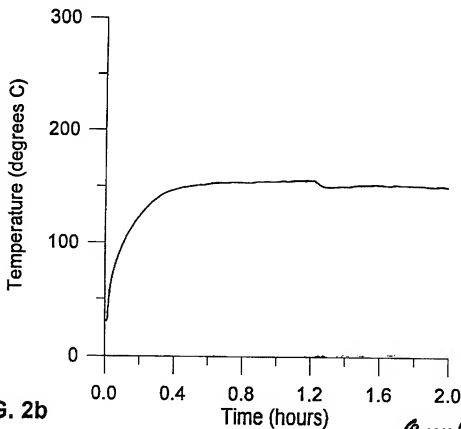


FIG. 2b

Owen Wiggs
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